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AD A001 E	ENTATIO	N PAGE	Form Approved OMB No. 0704-0188	
■ AD-A221 5	02 E 380	16 RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTO SITY APR 3 0 1990 2b. DECLASSIFICATION / DOWNGRA LINE SCHEDULE		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release Distribution unlimited		
4. PERFORMING ORGANIZATION REPORT NUMBER 5 8 Technical Report #8		S. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION 6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION		
Brigham Young University		Office of Naval Research		
6c ADDRESS (City, State, and ZIP Code) Department of Chemistry Provo, UT 84602		7b. ADDRESS(City, State, and ZIP Code) Department of the Navy Arlington, VA 22217-5000		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
Office of Naval Research			·	
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS	Transport transport	
800 No. Quincy Street Arlington, VA 22217-5000		PROGRAM PROJECT TASK NO. NO.	WORK UNIT ACCESSION NO.	
11. TITLE (Include Security Classification) Preparation of Chiral Diamido-, Dithionoamido- and Azapyridino-18-Crown-6				
12. PERSONAL AUTHOR(S) I.S. Bradchey, D. Hyggthy and D.M. Tanke				
J.S. Bradshaw, P. Huszthy and R.M. Izatt 13a. TYPE OF REPORT 13b. TIME COVERED 14. DATE OF REPORT (Year, Month, Day) 15. PAGE COUNT				
Interim FROM	то	April 20, 1990		
16. SUPPLEMENTARY NOTATION ACTUALIZATION TO CONTINUE				
17. COSATI CODES 48. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) FIELD GROUP SUB-GROUP C., roll Mark 1965, Element Continue on reverse if necessary and identify by block number) Subject Client Continue on reverse if necessary and identify by block number) Subject Client Continue on reverse if necessary and identify by block number) Subject TERMS (Continue on reverse if necessary and identify by block number) Subject Client Continue on reverse if necessary and identify by block number) Subject Client Continue on reverse if necessary and identify by block number) Subject Client Continue on reverse if necessary and identify by block number)				
Shiral dibenzyl-substituted pyridino-18-crown-6 ligands containing two amide (1, see Figure 1) and two thionoamide (2) moieties have been prepared by reacting the α,ω-diamine derivative of chiral dibenzyl-substituted tetraethylene glycol (5) with either dimethyl 2,6-pyridinedicarboxylate (7) or dimethyl 2,6-pyridinedithionodicarboxylate (8) (see Scheme I.). The physical properties for 1 and 2 are as follows: (S,S)-1; mp 131-132 °C; [α] _D -160.8° (c = 0.854, benzene); (S,S)-2; mp 138-139 °C; [α] _D -193.9° (c = 0.639, benzene). It is interesting to note that ligand 1 was converted to 2 by Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide]. The structure of 2 as determined by an X-ray crystallographic procedure has the bottom part of the macrocycle (away from the pyridine ring) in a puckered conformation. Compound 2 possibly can be reduced (desulfurized) by Raney nickel to give the chiral dibenzyl-substituted diazapyridino-18-crown-6 (X = H ₂). 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT □ UNCLASSIFIED/JUNILIMITED □ SAME AS RPI □ DIIC USERS 21 ABSTRACT SECURITY CLASSIFICATION □ UNCLASSIFIED/JUNILIMITED □ SAME AS RPI □ DIIC USERS 220 NAME OF RESPONSIBLE INDIVIDUAL CONTROLLED Classified Council Control Contr				
Dr. Harold Guard	Dr. Harold Guard (202) 696-4409			

Previous editions are obsolete. S/N 0102-LF-014-6603

SECURITY CLASSIFICATION OF THIS PAGE

Unclassified

Figure 1. Chiral diamido-, dithionoamido and azapyridino-18-crown-6

Scheme I. Preparation of chiral pyridino-crowns

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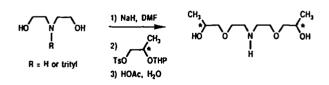
Chiral dimethyl-substituted azapyridino-18-crown-6 ligands (3 and 4) have also been prepared. Ligand 3 was prepared by reacting 2,6-pyridinedimethyl ditosylate (9) with chiral dimethyl-substituted azatetraethylene glycol (6) (see Scheme I) to give (S,S)-3; oil, $[\alpha]_D$ -4.26° (c = 2.702, benzene). Compound 3 was reacted with acetic anhydride to give 4; oil, $[\alpha]_D$ +31.2° (c = 0.5, benzene).

Ligand 3 formed a strong complex with α -(1-naphthyl)ethylammonium perchlorate. The ^1H NMR spectrum of the complex is very difficult to analyze suggesting that part of the complex has one proton from the ammonium salt transferred to the amine nitrogen atom of the aza-crown. Additional work is being done with this system.

Scheme II. Preparation of chiral starting diamine 5 and glycol 6

A. Diamine 5 was prepared as reported: Chadwick et al., <u>J. Chem. Soc., Perkin Trans. I</u> 1707 (1984)

B. Glycol 6



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